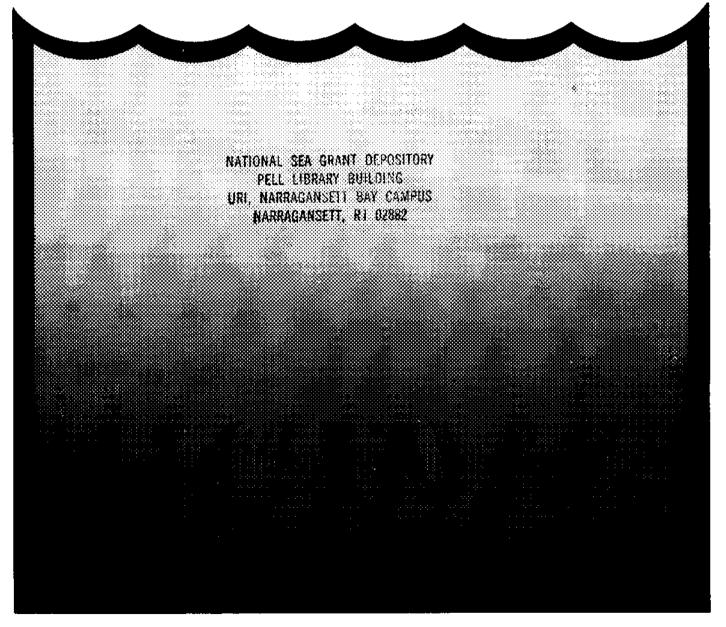
Trace Metal Environments near Shell Banks in Delaware Bay

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Sea C.L. Jepository



TRACE METAL ENVIRONMENTS NEAR SHELL BANKS IN DELAWARE BAY

Sea Grant Depository

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PREFACE

This report represents an interim record of progress during Fiscal Year 1972 in one aspect of the geological investigation of Delaware Bay. Preliminary interpretations have been included as well as appendices presenting the raw data.

The authors felt that the inclusion of a layman's definition of "part per million" would be beneficial in order to emphasize to all readers the magnitude of the numbers with which we deal in trace metals. Dale W. Jenkins, director of the ecology program in the Office of Environmental Sciences of the Smithsonian Institute contributed this definition. "The world's driest martini: one ppm of vermouth would be the equivalent of one ounce of vermouth in 7,800 gallons of gin." (Science, 177: pp. 476-77, 1972)

We thank Charles B. Weil and Roger D. Moose, of the Department of Geology, for taking the samples used, and Frederick K. Lepple, of the College of Marine Studies, for his assistance in the Laboratory and Data Reduction phases of this research.

The National Science Foundation, the National Oceanic and Atmospheric Administration, and agencies of the State of Delaware are free to use the contents in any way which serves the public interest, but are requested to respect the intention of the authors to publish the formal results of their investigation at a later date.



BACKGROUND

This paper reports the results of research for Fiscal Year 1972 into one aspect of the geological investigation of Delaware Bay. Biggs (1972) presented the results of a sedimentological survey of the oyster reef areas of Delaware Bay. Ninety-two discrete locations were sampled and analyzed for that study. The primary result of the survey was the observation that fine-grained sediments in Delaware Bay are concentrated to a large extent on the Delaware side of the bay. This led to the two-fold hypothesis that either the silts and clays have their source area along the Delaware shore, or there exist conditions for the preferential deposition of silt and clay sized particles along the Delaware shoreline, perhaps due to the Coriolis effect. While there is a vast amount of fine-grained material suspended in the coastal plain estuaries and in the nearshore waters of Delaware Bay, a reliable determination of its source has not yet been made. A corollary to the second hypothesis mentioned above provides the suggestion for a geochemical test of the hypothesis. That corollary was mentioned by Biggs (1972): "if extraneous materials (trace metals, pesticides, etc.) are attached to fine suspended particles, carried downriver, and deposited preferentially on the Delaware shore, then the Delaware side of the Bay is more susceptible to pollution sources from up-river."

INTRODUCTION

The primary objective of Fiscal Year 1972 research is to typify the trace metal geochemical aspects of the sedimentary environments which support oysters in Delaware Bay. These results would provide baseline information to be used in the oyster early-warning pollution monitoring system being developed by the State of Delaware and the University of Delaware under the auspices of the Sea Grant Program. A secondary objective of Fiscal Year 1972 research is to test the hypothesis outlined above. The tertiary objective of this project is an effort to characterize the trace metals determined with respect to 1) their generalized source (i.e., the Delaware River, the ocean, etc.), and 2) the primary factor(s) controlling their distribution.

Most of the original ninety-two samples used by Biggs (1972) had been kept frozen and were used for this research. In addition, twelve samples were obtained from viable oyster reefs in Delaware Bay (labelled B-1, B-2, and B-4 through B-13), and twenty-three samples were obtained which extended the area of investigation to the south and east (labelled SG-101-S-72 through SG-146-S-72). Table 1 is a listing of the positions of the samples from 118 discrete locations used in this project. Sampling and field handling techniques for all samples were those used by Biggs (1972). No sediment analyses are available for the newly procured samples. Figure 1 is a chart of the research area on which the sample positions are plotted.

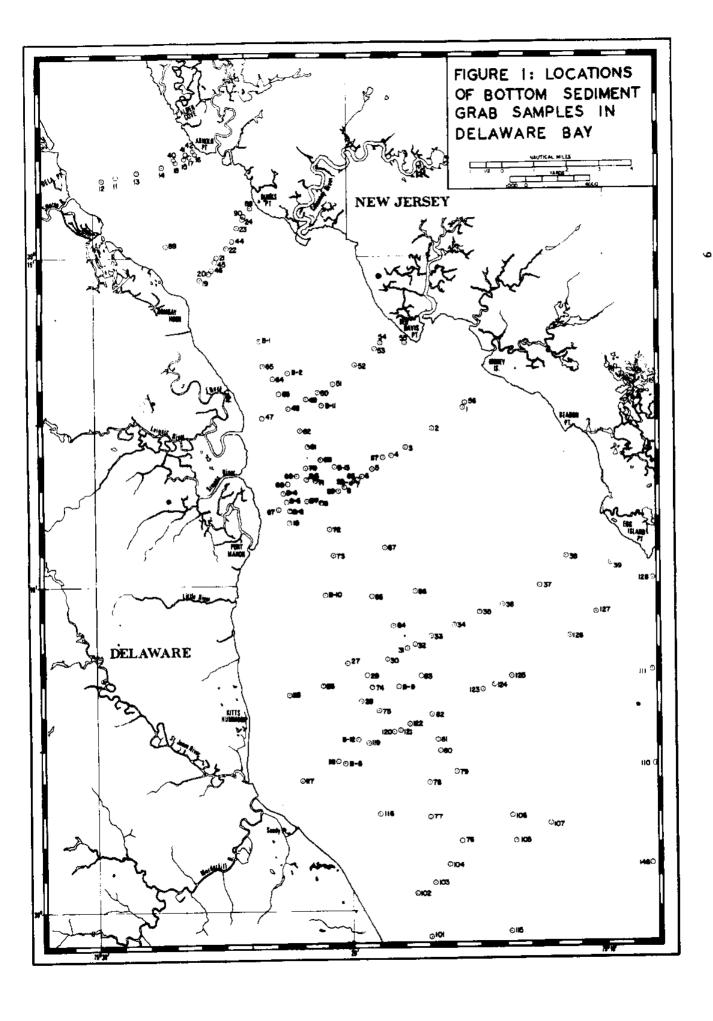
Table 1: Positions in Latitude and Longitude for Delaware Bay Bottom Sediment Grab Samples.

SAMPLE	LAT.	LONG.	SAMPLE	LAT.	LONG.
5G-1A-W-71	39-15.40	75-15,40	56-42-พ-71	39-23,20	75-26.00
56-18-6-71	39-15.46	75-15,46	SG-43-W-71	39-21,26	75-23.85
SC-2-W-71	39-14,76	75-16.75	SG-44-W-71	39-20-50	75-24.55
5G-4A-W-71	39-14.66	75-18.25	5G+45-W-71	39-19.90	75-25.20
53-48+b-71	39-14.06	75-18.25	SG-46-W-71	39-19,65	75-25.50
5G - 5-₩-71	39-13.60	75-19.65	5G-47-W-71	39-15,66	75-23.40
56-6-ฝ-71	39-13.35	75-19.55	SG-48-W-71	39-15.35	75-22.30
SG-7-₩-71	39-13.25	75-19.85	5G-49-W-71	39-15.65	75-21.75
SG-8A+W-71	39 - 13,10	75-20.20	SG-50-W-71	39-15.85	75-21.35
36-88-⊎-71	39-13.16	75-20.20	SG-51-W-71	39-16.18	75-20,60
SG-9+₩-71	39-12.60	75-21.05	SG-52-W-71	39-16.65	75-19.75
SG-10-W-71	39-11.95	75-22.2u	5G~53-₩-71	39-17.25	75-18.95
5G-11-₩-71	39-22.50	75.29.05	SG-55-₩-71	39-17.35	75-17.80
SG-12-W-71	39-22,40	75-29.65	SG-56-W-71	39-15.35	75-15.50
SG+14-₩-71	39-22.8L	75-27.30	SG-57-W-71	39-13.95	75-18.35
SG-15-₩-71	39 - 23.00	75-26.35	SG-59-W-71	39-13.00	75-20.35
SG-16-M-71	39-23.15	75-25.90	SG-60-W-71	39-13.90	75-21.16
5G-17-⊌-71	39-23.10	75-26.1u	SG-61A-₩-71	39-14.30	75.21.70
SG-18A-W-71	35-22.85	75-26.75	SG-618-W-71	39-14.30	75-21.70
SG-188-W-71	39-22.85	75-26.75	5G-62-W-71	39-14.8D	75-21.90
SG-19-₩-71	39-19.40	75-25,75	SG-63-W-71	39-15.85	75-22.7G
SG-20-W-71	39-19.60	75-20.75	5G-64-⊌-71	49-16.25	75-23.00
56-21-W-71	39-20.00	75 - 25,1G	SG-65-W-71	39-16.70	75-23.46
SG-22-W-71	39 - 20.25	75-24.75	5G-66-พ-71	39 - 1 3 , 30	75-19.70
SG-23-W-71	39-20.90	75-24,35	SG-67-⊌-71	39-12.35	75-22.75
5G-24-W-71	39-21.20	75-24.10	5G-68-W-71	39-13.05	75-22.40
5G-25-W-71	39-06.60	75-20.35	SG-70-W-71	39-13.60	75-21.70
SG-26-W-71	39-07.00	75-21.05	5G-71-W-71	39-13.25	75-21.30
SG-27-W-71	39-07.60	75-20.05	SG-72-W-71	39-11.75	75-20.75
SG-28-W-71	39-06-45	75-19.45	SG-73-W-71	39-10.95	75-20.60
SG-29-W-71	39-07.30	75-19.25	SG-74-W-71	39-06.90	75-19.1ն
SG-30-W-71	39-07.75	75-18.55	5G-75-⊎-71	39-06.15	75-18.85
SG-31-W-71	39-08,10	75-17.65	SG-76-W-71	39-03,95	75-16.95
SG-32-W-71	39-08.15	75-17.45	SG-77-W-71	39-02.85	75-16.90
5G-33-W-71	39-08.40	75-16.65	SG-78-W-71	39-u2.05	75-15.65
5G-34-W-71	39-08.75	75-15.85	5G-80-W-71	39-04.95	75-16.50
56-35-W-71	39 - 09.05	75-14.75	5G-81-U-71	39-05.20	75-16.85
SG-36-พ-71 SG-37-พ-71	39-09.35	75-14.10	5G-82-W-71		75-16.80
SG-39-W-71	39-10,10	75-12.50	SG-83-W-71		75-17.20
5G-40-W-71	39-10.76	75-09.80	SG-84-6-71		75-18.25
5G-41-W-71	39-23.uU 39-25.15	75-26.85	SG-85-W-71	39-89,70	75-19.10
	79-53-13	75-26.20	5G-86-⊎-71	39-09.80	75 - 17.40

Table 1 (cont.)

PHILOSOPHY, AND THE CONCEPT OF ENVIRONMENTAL ACTIVITY

The basic philosophy subscribed to in undertaking this research is that the trace metals which are of interest are only those which are available for introduction to the marine food web through naturally occurring biological or chemical processes; i.e., those trace metals which are "environmentally active." Those cations so firmly bonded to-, or exchanged within-, mineral grains that natural biochemical processes cannot remove them are of no concern to this investigation. The laboratory extraction procedure used was designed to approximate, however crudely, the severest conceivable naturally occurring biochemical conditions, without completely degrading the sediments.



It must be borne in mind, however, that any given sediment particle enters our laboratory extraction system only once, and then is gone from consideration. In Delaware Bay it is possible for the resident epi- and infauna to recycle the top few centimeters of sediment several times each year, thereby making each particle in the natural habitat available for cation stripping at the very least more than once (see also: Gordon, 1966; and Rhoads, 1963, for examples in other estuarine systems). This is partial justification for making the treatment used here as severe as it is. In addition to this is the fact that the extraction technique used here is a simple, reproducible, inorganic process, whereas the gut-chemistry of even the simplest biological specimen is a complex scheme of enzymes, catalysts and organic acids. The results of the inorganic technique used here are generalized and have a wide range of applications, whereas the results of a biochemical extraction would be species-specific and, therefore, of limited use.

For the purpose of this research the environmentally active trace metals are defined to be those cations which can be separated from 3 grams of dried and disaggregated sediment, from the silt and clay fraction, by leaching with 500 mls, of 10% (vol/vol) HCl in distilled/deionized water at 70°C for 96 hours.

LABORATORY PROCEDURES

General: All solutions used in handling, separating, extracting and analyzing the samples were prepared using distilled/deionized

water, or Fisher Certified A.C.S. solvents. With the exception of a 3-inch, 63-micron sieve, all laboratory equipment and utensils used in the handling of the samples were made of polyethylene or other plastic, or of ceramic, in order to eliminate, insofar as is economically practical, the probability of outside contamination. All chemicals used in the analyses were Fisher Certified A.C.S. Reagents, and all standard solutions were prepared from Fisher Certified Atomic Absorption Standards.

Silt and Clay Separation: A subsample of each of the samples, wet weight approximately 250 grams, was transferred to an acidwashed, double AA-water-washed, 600 ml. plastic beaker. ("AA-water" is used interchangeably with "distilled/deionized water.") AA-water was added and the sample aggitated until suspended. The suspensate was passed through a U. S. Standard No. 230, 63-micron mesh sieve, and was collected in an acid-washed, double AA-water washed, 1 liter polyethylene bottle. Then the collected suspensate was centrifuged at maximum RPM in a Universal Model UV Centrifuge, using Nalgene tubes, for 30 minutes. The supernatant, containing some non-separable colloids, was discarded. The sediment particles were transferred to a 50 ml. plastic beaker and dried at 70°C. The dried sediment was milled to uniform size, determined only by visual approximation, in a Spex Industries Model 8000 Mixer Mill, using a ceramic powder vial and ball. The resulting powder was transferred to a plastic vial, capped and stored.

Trace Metal Extraction: Polyethylene 500 ml. bottles were pretreated by leaching with 10% (vol/vol) HCl at 70°C for 96 hours immediately prior to use for trace metal extractions. Subsamples of the dried and disaggregated silts and clays were weighed out at 3.00 ± 0.001 grams using a Mettler Analytical Balance. The weighed samples were transferred to the acid-treated bottles and 500 mls. of 10% (vol/vol) HCl were added. The acid was prepared by diluting 50 mls. of concentrated HCl (sp. gr. = 1.19) to 500 mls. with AA-water, in order to avoid error due to the electrostriction of the AA-water by the addition of chloride ion. The bottles were capped tightly, shaken vigorously, and heated at 70 - 4°C for 96 hours. The bottles were shaken and vented periodically during the course of the heated extraction. When 96 hours had elapsed the solutions were vacuum filtered while hot using a Millipore filtration apparatus with AAWP 0.8 micron filters. The supernatant was returned to the washed bottle in which it had been extracted, capped and stored in a cool place pending analysis.

ANALYTICAL CONDITIONS

General: All analyses were conducted using a Jarrell-Ash Model 800 Atomic Absorption Spectrophotometer in association with twin Honeywell Electronik 17 single-event pen recorders set for 15-inches per hour chart speed. Response of the recorders was 1 second for 1 millivolt full-scale deflection. Hollow cathode lamps used for atomic absorption were all single-element, high spectral output, Jarrell-Ash lamps.

The extraction technique used was designed to yield trace metal concentrations within the direct-reading limits of the spectro-photometer for most of the metals of interest. Background corrections were investigated on a routine basis, but no significant differences were noted between corrected and uncorrected readings. As the use of the background correction, B/A mode, reduced the signal-to-noise ratio, it was not used.

Iron: Iron concentrations were extremely high in the extraction solutions. A secondary absorption line was selected to allow accurate determinations to be made. The following analytical conditions prevailed during the analysis for iron:

> Lamp Current 8 ma , Wavelength 3720 Å 2.00 (arbitrarily set) RB 1.96 MΒ -311HVB Exit Slit Pair 900-1000_µ % Absorption--Direct Mode 3 (1-3 scale of Damping reducing noise) 10 cm. Burner Slot air = 15 scfhFlame acetylene = 4 scfh aux. air = scfh $0.01 \, \mu g/m1$ Detection Limit \pm 0.05 µg/m1 Sensitivity

Magnesium: The magnesium concentrations encountered were too high to allow the use of the primary 2852 Å line, and they were too low to allow reliable use of the secondary 2025 Å line in the % Absorption mode. Therefore, the Absorbance mode was adopted using the primary wavelength to allow for raising the upper detection

limit. The following analytical conditions prevailed during the analysis for magnesium:

10 ma Lamp Current 2852 Å Wavelength 2.00 (arbitrarily set) RB MB 2.00 HVB -34075-100u Exit Slit Pair Absorbance--Direct Mode 3 (1-3 scale of Damping reducing noise) 10 cm. Burner Slot air = 15 scfh Flame acetylene = 4 scfh aux. air = 4 scfh $0.0004 \, \mu g/m1$ Detection Limit $\pm 0.004 \, \mu g/ml$ Sensitivity

Zinc: These analyses were routine with no unusual conditions. The following analytical conditions prevailed during the analysis for zinc:

Lamp Current 7.5 ma 2139 Å Wavelength RB 2.00 (arbitrarily set) 2.00 ΜB -470HVB 75-100µ Exit Slit Pair % Absorption--Direct Mode 3 (1-3 scale of Damping reducing noise) 10 cm. Burner Slot · air = 15 scfhFlame acetylene = scfh aux. air = scfh $0.003 \, \mu g/ml$ Detection Limit \pm 0.015 µg/ml Sensitivity

Chromium: The signal-to-noise ratio for chromium at the concentrations encountered in most of the extraction solutions made the use of the % Absorption Mode unreliable. The Concentration mode with full signal expansion was adopted, along with maximum damping at the pen recorder in complement of the maximum damping at the spectrophotometer signal output. The following analytical conditions prevailed during the analysis for chromium:

10 ma 3579 Å
2.00 (arbitrarily set)
2.00
-390
150-200µ
Concentration10 (maximum)
3 (1-3 scale of reducing noise)
10 cm.
air = 15 scfh
acetylene = 4 scfh
aux. air = 4 scfh
0.005 μg/m1 + 0.06 μg/m1

<u>Copper</u>: The concentrations of copper encountered in the extract were in the lower end of the reliable detection range. In order to overcome the low signal-to-noise ratio, the lamp current was raised above the normal operating currents, and exit slits were opened wide to allow the maximum throughput of energy. The following analytical conditions prevailed during the analysis for copper:

Lamp Current	15 ma_
Wavelength	3247 Å
RA	2.00 (arbitrarily set)
MA	1.36
HVA	-330
Exit Slit Pair	900–1000µ
Mode	<pre>% AbsorptionDirect</pre>
Damping	3 (1-3 scale of
	reducing noise)

Burner Slot

Flame

air = 15 scfh
acetylene = 4 scfh
aux. air = 4 scfh

Detection Limit

Sensitivity

10 cm.

air = 15 scfh
acetylene = 4 scfh
aux. air = 4 scfh
0.003 µg/ml
± 0.04 µg/ml

<u>Lead</u>: The concentrations of lead encountered in the sediment extract were in the lower limits of reliable detection. However, use of the secondary 2833Å line was required because the signal-to-noise ratio on the primary 2170Å line approached unity. Despite the low signal-to-noise ratio, reproducible standard curves were recorded on three occasions using the secondary wavelength. No further steps were taken to enhance the signal. The following analytical conditions prevailed during the analysis for lead:

Lamp Current 5 ma Wavelength 2833 Å RA 2.00 (arbitrarily set) MA 1.75 HVA -490 Exit Slit Pair 150-200µ Mode % Absorption--Direct Damping 3 (1-3 scale of reducing noise) Burner Slot 10 cm. air = 15 scfhFlame acetylene = 4 scfh aux. air = 4 scfh $0.03 \mu g/m1$ Detection Limit \pm 0.30 µg/ml Sensitivity

<u>Cadmium</u>: The concentrations of cadmium encountered were so low as to discourage any confidence in the data. Signal-to-noise ratio in these concentrations is virtually 1, with several samples registering concentrations equal to the Detection Limit for direct reading. Attempts to use the concentration mode only served to

lower the signal-to-noise ratio further. Despite the low level of confidence in the data, the method did yield reproducible standard curves, and so the results are presented. The following analytical conditions prevailed during the analysis for cadmium:

Lamp Current 8 ma Wavelength 2288 A RB2.00 (arbitrarily set) MB 1.90 HVR -540 Exit Slit Pair 425-500_u Mode % Absorption--Direct Damping (1-3 scale of reducing noise) Burner Slot 10 cm. Flame air = 15 scfhacetylene = 4 scfh aux. air = 4 scfh Detection Limit $0.003 \, \mu g/m1$ Sensitivity \pm 0.02 µg/m1

Mercury: Mercury analyses were performed using a flameless, cold vapor technique, in which a quartz cell replaces the burner head. The quartz cell is aligned in the optical beam path, and is attached to a compressed air circulatory system and a series of gages and stopcocks. The system was purged by running air through the plumbing into the quartz cell and venting while the spectrophotometer was tuned. Two-ml aliquots of the extraction solution were pipetted into ground glass reaction vessels. Mercury bound inorganically within the solutions was reduced to elemental Hg by the addition of 0.3 ml stannous chloride solution (20% wt/vol in concentrated HCl). The elemental mercury was carried by the air stream into the quartz cell. The flameless vapor technique is highly sensitive, and has an upper limit of reliability of

200 nannograms of mercury per aliquot. Reliable concentrations of Hg were read in the 0.2-5.0 ppb range. Calibration was accomplished with a 10 ppb standard, and linearity was assumed between zero and 10 ppb. The following analytical conditions prevailed during the analysis for mercury:

5 ma
2537 Å
2.00 (arbitrarily set)
1.87
-395
900–1000μ
Concentration10 (maximum)
3 (1-3 scale of reducing noise)
0.5 scfh
0.2 nannograms/ml
± 0.15 nannograms/ml

Nickel: In trying to analyze for nickel by direct aspiration the signal-to-noise ratio approached 1 in all modes of operation. An evaporation was carried out which yielded a 2.5% concentrated solution. The flame was tuned down to extremely lean conditions, and no auxilliary oxidant was used. These measures brought the signal-to-noise ratio to within acceptable limits, and reliable results were obtained. The following conditions prevailed during the analysis for nickel:

Lamp Current	10 ma
Wavelength	2320 Ă
RA	2.00 (arbitrarily set)
MA	1.80
HVA	-620
Exit Slit Pair	75-100μ
Mode	% Absorption Direct, 2.5X
Damping	3 (1-3 scale of
• 0	reducing noise)

Burner Slot 10 cm. Flame air = 15 scfh acetylene = 2 scfh aux. air = 0 scfh Detection Limit $0.01 \mu g/ml$ $0.1 \mu g/ml$

Strontium: Analysis for strontium was carried out in the flame emission mode, using a nitrous oxide/acetylene flame. The signal-to-noise ratio was moderately favorable and reasonable reproducibility of the standard curves was attained. However, a gradual decline in sensitivity was noted as analyses proceeded. The manufacturer provides no sensitivity specification for metals detected by flame emission—it was assumed that the sensitivity was one order of magnitude more coarse than the detection limit. The following analytical conditions prevailed during the analysis for strontium:

4607 Å Wavelength Mode Flame Emission Flame nitrous oxide = 9 scfh acetylene = 6 scfh aux. $N_20 = 4$ scfh Zero Setting 3.08 Sensitivity Setting 7.66 Detection Limit $0.005 \, \mu g/m1$ \pm 0.05 μ g/ml Sensitivity

EMISSION SPECTROPHOTOMETRY

Prior to accomplishing the analyses outlined above, it was desirable to determine gross presence-absence, and rough approximations of concentrations, of the trace metals of interest here.

Of the many methods available to determine total chemistry of a

sediment sample, emission spectrophotometry was chosen. The new samples from the oyster reefs were separated as described above, and small amounts of each of these samples were sent to the E. I. DuPont de Nemours Co., Wilmington, Delaware for emission spectrophotometric determinations. Along with these samples were sent samples of bottom sediments from each of the larger tributary tidal estuaries which empty into Delaware Bay, and samples of dried oyster tissues from each of the 25 sites sampled. The results of emission spectrophotometric determinations are tabulated here in Appendix A.

RESULTS

Table 2 contains a tabulation of all the concentrations of trace metals determined during Fiscal Year 1972 research. These concentrations are expressed as micrograms per gram, or parts per million, of sediments finer than 63 microns.

The values presented in Table 2 were used to plot the geographic variations among the ten metals determined on the chart of the research area presented as Figure 1. Figures 2 through 11 are plots of the geographic variations in Delaware Bay bottom sediments of iron, magnesium, zinc, chromium, copper, lead, cadmium, mercury, nickel and strontium, respectively. Contour intervals for each plot were chosen to satisfy the following conditions: 1) contour intervals had to be of a uniform interval, 2) they had to bracket approximately 90% of all the data, and 3) the intervals had to be broad enough to illustrate general trends without the introduction of specific

Table 2: Concentrations of Trace Metals in Delaware Bay Bottom Sediments, Expressed as Parts Per Million of the <63 micron Sediment Fraction. (Mercury listed in PPB)

SAMPLE	Fe	Mg	<u>Zn</u>	<u>Cr</u>	<u>Cu</u>	<u>Рь</u>	<u>Cd</u>	Но	N1	Sr
SG-1A-⊌-71	34 500	6850	388	113	96	103	3.8	908	625	161
SG-18-W-71	39350	8000	495	127	68	107	4.2	983	725	16ü
5G-2-W-71	43350	9400	475	133	43	1u3	2.5	975	895	130
SG-4A-W-71	44000	7950	168	180	34	73	2.5	708	600	117
5G-48-W-71	32650	4156	78	33	9	50	Ū, B	113	625	56
SG-5-W-71	42350	7400	522	117	65	167	3.3	1142	850	117
5G-6-W-71	49150	6650	363	113	58	127	2.2	958	1167	7U
SG-7-W-71	42650	7150	435	1,00	U()	117	2.7	792	175	110
SG-8A-W-71	45000	6500	400	92	85	167	2,5	1291	1035	53
SG-8 8- W-71	44000	7950	413	86	62	113	2.5	917	225	94
SG-9-W-71	42850	8500	5ևև	111	47	103	4.2	917	770	114
SG-10-W-71	37150	7550	317	80	34	83	2.2	783	592	165
S5-11-ม-71	28500	4400	278	1 3iu	50	157	2.5	750	478	53
5G-12-W-71	3315G	3850	290	113	43	162	1.7	825	492	46
58-14-5-71	300au	6850	1875	119	163	250	6.3	1783	650	46
50-15-6-71	42150	5400	875	150	108	200	3.8	792	675	46
. SS -16-⊍-71	33650	3700	67	95	86	54	1.0	133	525	32
SG-17-W-71	32500	425U	345	108	43	93	2.5	358	358	52
SS-18A-W-71		6900	110u	133	74	208	5.5	1350	775	67
SG-188-W-71	4 7 500	7050	558	161	102	152	1.0	783	775	59
SG-19-0-71	17350	2650	48	80	50	25	6.0	133	295	48
5G-20-W-71	39350	4050	287	150	50	76	1.6	783	500	53
SD-21-M-71	43150	8400	160	83	18	25	0.8	86	417	56
50-22-W-71	26850	4850	80	62	18	20	0.8	108	342	48
SD-23-M-71	41500	4100	1200	15ն	75	265	2,5	2275	525	155
SG-24-W-71	5765D	7400	2667	282	98	1063	3.3	975	1717	121
5G-25-6-71	37150	6250	288	120	25	73	2.2	725	545	62
SG-2S-10-71	37650	7550	317	153	40	167	1.5	558	403	59
55-27-W-71	32650	5850	357	133	43	88	2.5	1292	425	80
56-28-ม-71 56-29-ม-71	37250 32860	7000	4նև 342	192 153	115	184	3.7	536	592	77
50-30-6-71 50-30-6-71		7300	217	168	L ()	54	Ü.8	583	367	210
SG31+0+71	24500 35650	4650	442	175	2 <u>8</u> 43	4,44 6.≅	U.6	500	283	56
5G-32-W-71	3665 0	72 5 0	353	212	43	58 73	1.7	725	358	75
SG-33-W-71	38150	7500	310	247	52	163	2.5	au 8	462	75
55-34-W-71	52000	9150	683	268	65	157	4,3	583	545	267
56-35-W-71	41250	10250 8650	312	209	43	96	2.5	2150	873	155
Su-36-W-71	41250	9150	412	187	21	113	2,2	863	717	144
SG-37-W-71	27350	8150	435	199	269	167	4.3	7 6 6	808	94
56-39-6-71	35350	8100	637	139	40	167 166	4.5	1199	617	506
SG-6G-W-71	47150	5150	222	167	62	63	3.2	833	65Ü	205
12.112.GB	-,150	חרדר			Ų.	٠,	J + E	371	833	45

Table 2 (cont.)

SAMPLE	<u>fe</u>	Mg	<u>Zn</u>	<u>Cr</u>	Cu	<u>Pb</u>	<u>Cd</u>	<u> </u>	Ni	<u>Sr</u>
SG-41-W-71	36000	6250	166	179	86	73	2.ن	86	583	40
5G-42-W-71	3785Ն	63ut.	11 u	158	123	78	1,5	20և	378	38
SG-43-6-71	45656	75 uu	833	249	77	267	2,3	1625	1045	148
56-44-W-71	50000	7800	5833	447	252	890	11.3	1666	3633	520
56-45-W-71	270an	5750	83	208	18	47	2.2	156	608	43
56-46-W-71	285U0	425U	203	216	86	142	1.5	725	608	32
SG-47A-W-71	33560 ·	5550	267	159	68	217	2.3	600	617	32
SG-478-W-71	265სს	4400	192	148	28	68	2.2	408	625	27
5G-46-W-71	34666	76UU	3 U5	193	33	78	1.5	642	637	112
SG-49-W-71	31 50L	665ü	383	185	43	73	1.5	6 00	762	107
5G-5U-W-71	43350	8450	525	258	58	225	3.5	875	925	121
5G-51-W-71	41850	10.50	408	205	56	183	3,2	2058	750	235
5G-52-W-71	32606	61 են	167	148	22	59	1.0	183	670	70
SG-53-W-71	440UL	8900	440	277	171	375	2.3	1750	943	154
SG-55-W-71	3125U	4400	95	250	260	250	1.5	938	463	23
5G-56-W-71	3685U	7 050	1.65	227	1 35	37	0.8	1 սն	5 5 0	15
SG-57-W-71	33350	6550	90	256	34	21	1.5	128	568	32
5G-59-W-71	28850	5750	33 4	184	40	88	1.5	750	537	43
SG-60-W-71	37000	7850	442	362	₿Ü,	2u8	2.2	1058	692	93
5G-61A-W-71	37 u i.ii	7550	422	28u	68	131	2.2	1917		74
5G-618-W-71	2885ú	465U	125	110	47	88	1.0	371	667	23
SC-62-W-71	30850	52սև	3 25	2นน	71	63	2.0	630	500	27
SG-63-W-71	40650	8700	375	185	47	88	2.3	558	492	83
SG-64-W-71	3835G	69UD	103	128	77	37	1.0	228	570	27
SG-65-W-71	4135ե	7նեն	595	174	256	242	1.0	625	775	32
SG+66-W-71	45150	8350	1042	265	71	200	3.2	2916	767	68
SG-67-W-71	26000	5600	325	143	40	47	1.5	350	453	37
5G-68-W-71	25000	4600	242	167	38	83	0.6	433	442	78
5G-70-W-71	24150	3 7 60	96	178	47	68	1.0	175	375	74
SG-71-W-71	2865u	4700	588	216	68	146	1.7	458	528	74
SG-72-W-71	31 Lúu	69 00	35U	188	4(1	124	2.5	562	428	78
SG-73-W-71	2915C	6300	458	158	28	93	2.5	562	442	78
56-74-W-71	15900	4100	267	145	49	56	2.5	197	183	146
SG+75-W-71	44500	9150	483	2L6	89	155	2.7	96	6u 3	205
SG-76-W-71	38350	905u	262	193	56	88	2.7	1458	508	2ū5
SG-77-W-71	4200L	82úu	42Li	276	49	131	3.3	1442		140
56-78-W-71	20650	2650	138	227	25	66	2.0	1L33	303	41
SG-80-W-71	5485G	9900	37 2	392	100	183	3.3	1768	742	215
SG-81-W-71	67250	16500	560	196	109	300	3.B	4413	1038	219
56-62-W-71	5515ú	9150	640	267	63	241	3,3	1375	903	230
5G-83-W-71	41150	835û	373	267	63	111	2.0	691	658	109
5G-84-W-71	23850	4460	237	160	46	88	2.0	113	370	157
SG-85-W-71	26650	445b	222	25U	35	66	1.7	408	433	99
5G-86-W-71	26750	49ùti	200	250	48	91	2.5	267	363	125

Table 2 (cont.)

BAN EL	Fe	Mg	Zπ	Сr	Cu	Ρb	<u>Sd</u>	<u>ਜ਼</u> ਰ	Ni	<u>5r</u>
SS-87-W-71	31833	5560	292	2U3	73	138	1.7	475	475	93
50-68-W-71	3856ü	8650 J	BUL	340	54	268	4.17	4'7UO	455	522
5G+69-W-71	3165Ե	51.00	96	16u	4.3	26	1.3	161	425	60
5G-90-W-71	4 6 566	51 til	212	232	143	292	1.0	A 75	742	5Ù
56-101-5-72	3uB5u	6850	233	118	49	83	1.3	อวโม	475	5ს
56-102-5-72	38350	845U	29D	227	63	118	2.0	475	476	125
56-103-5-72	32 35 ù	71.50	2. 3 U	232	59	95	1.7	35û	4 63	125
SG-104-S-72	37 uub	72სს	295	238	86	188	1,7	25ს	478	140
56-105 - S-72	42350	766 u	283	205	ь3	111	2.0	31.3	608	161
SG-107-S-72	32 25 0	8u50 :	243	245	84	99	3.8	345	438	763
5G - 110-S-72	27650	6350	2 17	155	333	155	1.3	325	403	93
56-111-5-72	3 <u>0,5</u> 00	9ննե	_ بانا3	355	95	1.38	2.0	590	- 51 ե	535
SG-115-S-72	3 6 500	8050	225	197	49	63	1.3	31.3	542	140
SG-116-S-72	42350	16850	525	214	225	188	1.7	396	692	297
56-117-5-72	26000	5000	202	113	32	83	1.0	650	3 03	64
SG-118-5-72	26 6 50	5200	2L 3	19u	39	88	1.0	288	358	97
5G-119-6-72	24650	560Ს	265	125	49	95	1.0	458	342	64
5G-12U-5-72	23000	5 1 ບປ	175	118	35	99	U.7	371	358	69
SG-121-5-72	35650	7400	3UG .	178	53	208	1.0	35ú	487	178
5G -1 22 - 5-72	635üü .	9766	42b	313	84	468	2.0	433	905	140
SG-123-S-72		7u50	343	208	56	131	1.7	360	525	. 89
5G-124-3-72		9650	485	3u3	93	250	2.5	417	542	272
SG-125-5-72	26500	6150	223	143	39	165	1.3	32 5	342	125
SG-126-S-72		8650	400	13u	76	124	1.0	40 8	6UL !	248
SG-127-S-72	24856	E 350	303	178	89	195	3.3	313	320	751
SG-128-5-72	3 365 0	665U	183	150	76	105	1.7	35D	283	78
55-146-5-72	44150	8650	31.3	197	50	175	1,3	328	537	156
81	28350	4700	143	140	18	31	1.7	248	403	45
B2	365uU	5150	372	184	76	118	1.3	550	512	64
B4	32850	69üü	283	124	35	83	1.3	338	467	64
B 5	3365L	695ü	338	163	39	118	1.3	<i>5</i> 28	428	74
86	3235ü	6450	280	130	39	165	1.7	242	353	89
87	31 (10)	5966	33B	178	53	83	1.0	208	320	69
88	3บ35ปี	6500	2 37	103	35	77	1.7	383	342	93
E9	29850	6600	265	114	56	72	5.0	733	458	115
B16	3485U	7400	327	187	79	118	2.u	4ป5	487	93
611	34350	62LU	77	1 30	25	41	1.7	153	492	55
812	35650	6600	362	145	56	111	1.7	478	475	60
913	25850	5400	205	140	25	66	1.3	277	392	60

trends which may or may not be capable of substantiation.

SOURCES OF ERROR

With any tedious and repetitive laboratory process there are always ample opportunities for contamination of a sample or two by simple human error. The errors which are most costly, however, are those arising from faulty design of the test procedures. In the procedures used here there are at least five places where significant error may be introduced, either in the form of contaminants or in analytical error. The four major sources of consistent contamination probability are as follow: 1) use of distilled/deionized water which has been contaminated or improperly distilled, 2) contamination due to contact of the sample with the metal sieve during sample preparation, 3) loss of metals due to the discarding of the colloid-containing supernatant after centrifuging, and 4) contamination from the millipore filter during the filtration of the hot extraction solutions. Each of these four sources was tested for detectable contaminant levels.

Five hundred ml aliquots of the solutions from each of the possible contaminating steps were measured into 1 liter volumetric flasks. The pH was adjusted to 2.8 by the addition of Bromphenol Blue indicator and the dropwise addition of concentrated HCl. A chelation-extraction yielded a fifty-fold concentration of the metals present due to contamination. Ten ml of 1% Ammonium Pyrrolidine Dithiocarbamate (APDC) were added, shaken vigorously

and allowed to react for 15 minutes. The metal-APDC chelates were extracted with 10 ml of Methyl Isobutyl Ketone (MIBK) and the ketone layer aspirated directly into the flame of the spectrophotometer. Several of the metals with high concentrations in the bay were analyzed for—iron, magnesium, zinc, and nickel—with negative results in all but the colloid-discarding sample. However, the level noted was not inordinately high—on the order of several hundred ppb iron, several tens of ppb magnesium, traces of zinc and no nickel. Considering that the sample preparation was carried out on samples still containing bay water, these metal levels probably represent ions from the bay pore waters taken into solution during sample preparation.

A one-liter aliquot of the colloid-discarding supernatant solution was vacuum filtered using a Millipore filtration apparatus with an HAWP 0.45 micron filter. The retained particulate material weighed 0.0017 grams, or 0.006% of the nominal yield of 30 grams of fine grained material from the sample preparation procedure previously described. This is well below the 0.03% error already found acceptable in the extraction technique previously described, and, therefore, is not considered to be an important source of error.

The last source of error is the machine error caused by resolution limitations inherent in the design of the atomic absorption spectrophotometer. Listed in the analytical conditions for each metal was the "sensitivity," or resolution limit of the machine. In converting the concentration readings determined for the extraction

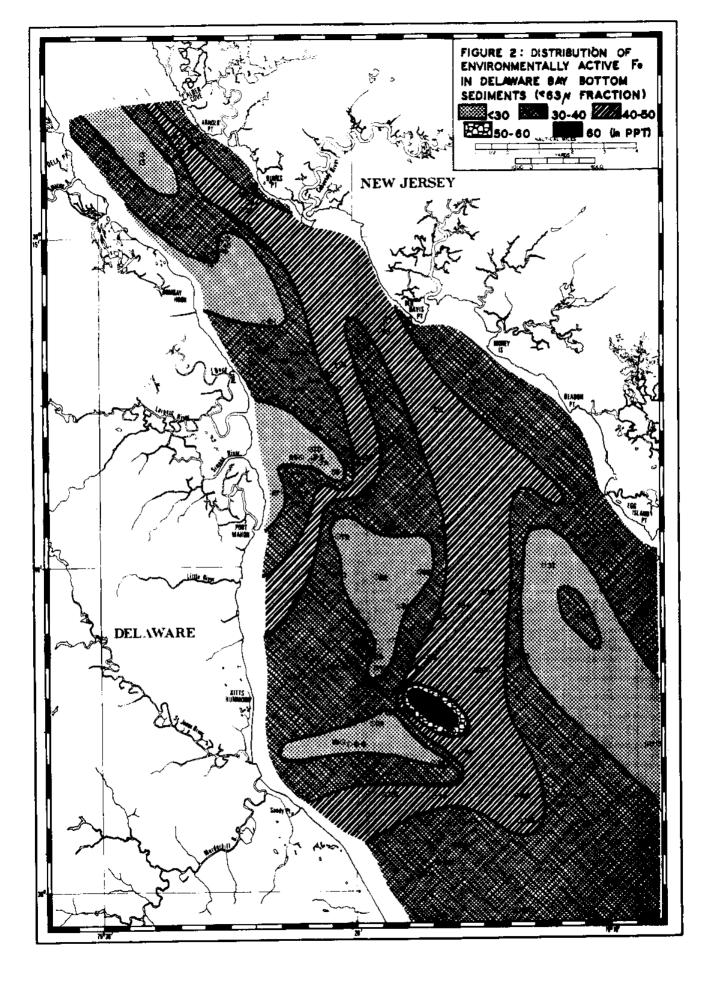
solutions into concentrations in the finer than 63-micron fraction, the conversion factor of 1/3 was used. Table 3 is a tabulation of the manufacturer's specifications for sensitivity. These specifications were met for all metals except Fe and Mg, since all readings were made by direct determination.

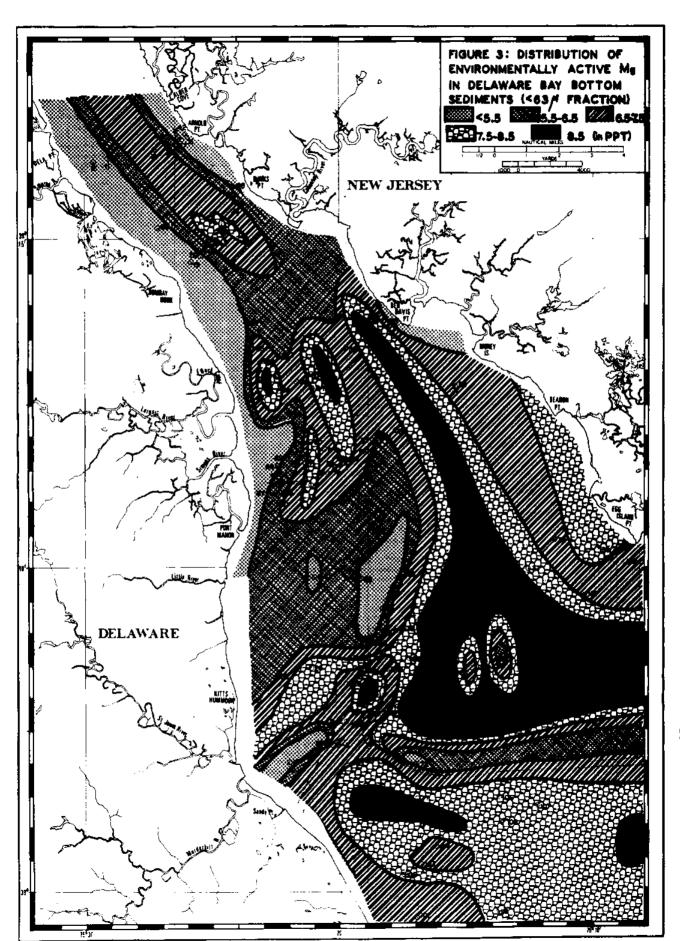
Table 3: Sensitivities for the Data Presented in Table 2, Expressed as [±] Parts Per Million of the <63 Micron Sediment Fraction.

Metal	Sensitivity
Fe	0.05 ppm
Mg	0.004 ppm
Zn	0.015 ppm
Cr	0.06 ppm
Cu	0.04 ppm
РЪ	0.30 ppm
Çd	0.02 ppm
Hg	0.15 ppb
Ni	0.10 ppm
Sr	0.05 ppm

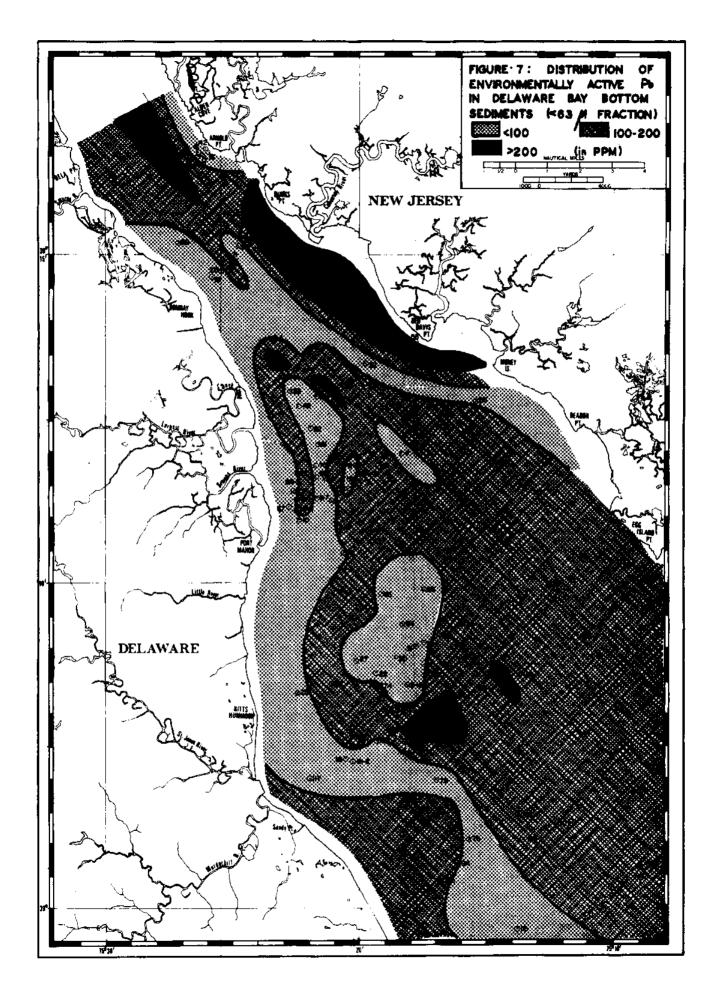
DISCUSSION

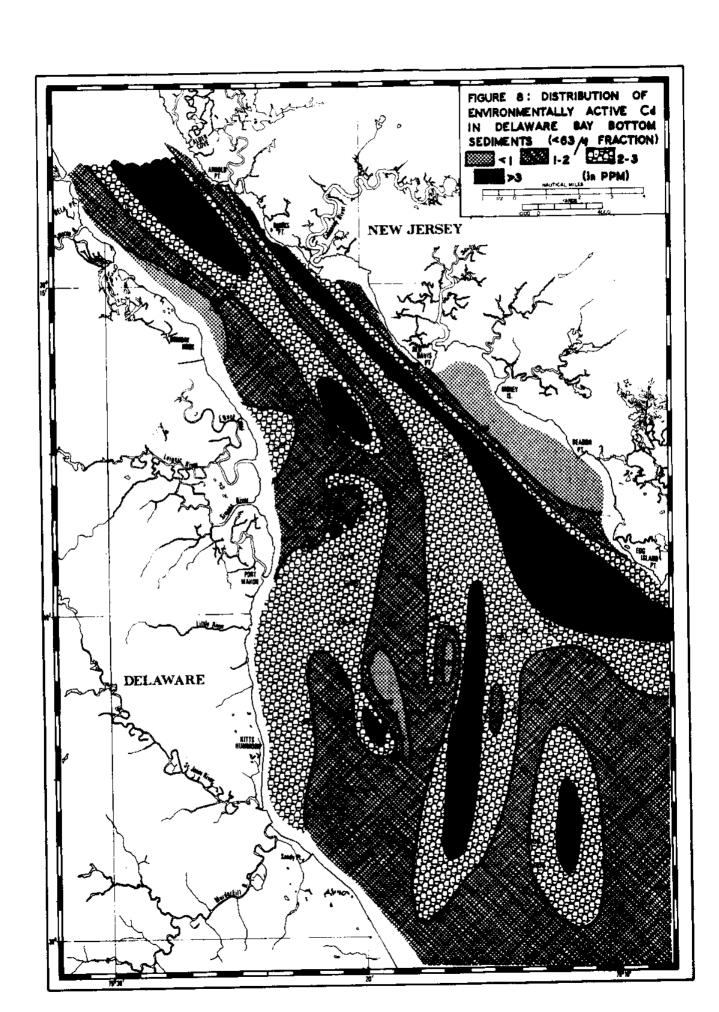
When one looks over Table 2 and Figures 2 through 11, one is immediately struck by the extremely high values obtained for iron and magnesium. There are a number of factors influencing the high levels of iron and magnesium, and also their distribution around the Bay. The greatest influence is the fact that chlorite, which is one of the more common clay minerals in Delaware Bay bottom sediments, is soluble in hydrochloric acid. One would expect that iron and magnesium would be in high concentration because both are primary constituents of chlorite. However, one is struck by the great

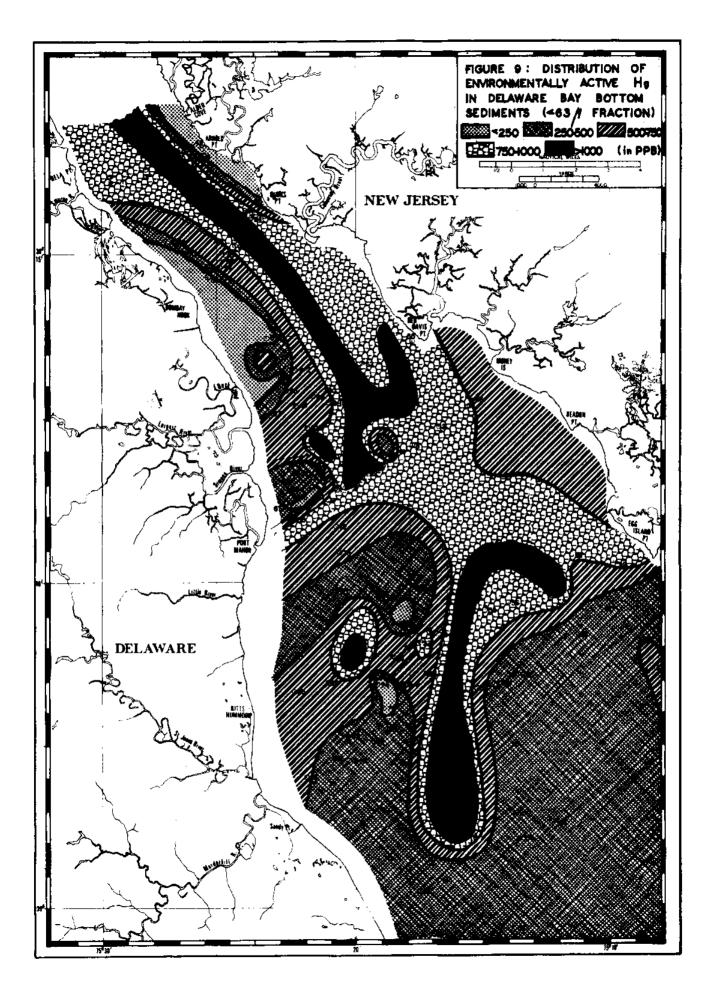


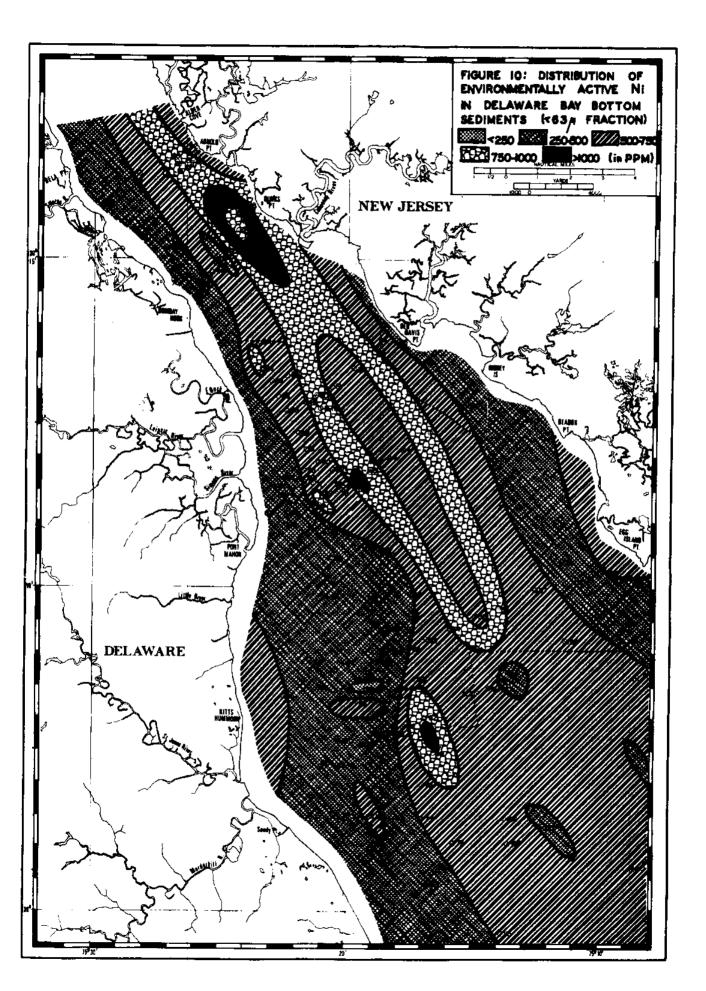


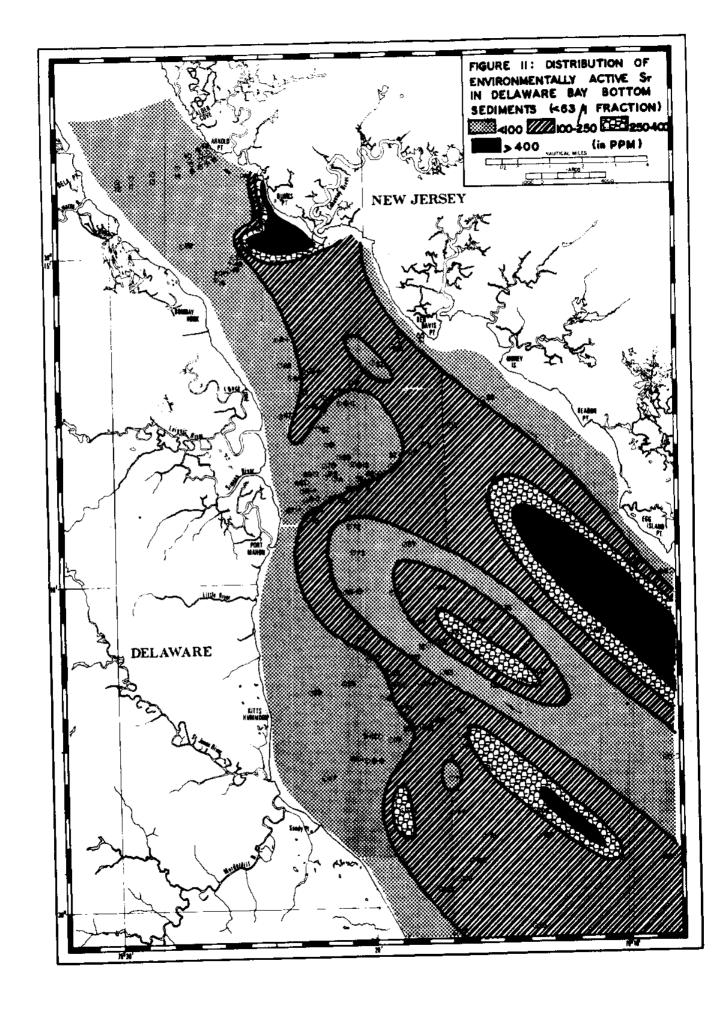












dissimilarity of the two regional diagrams presented as Figures 2 and 3. It seems apparent that the iron source is from the Delaware River, while the magnesium source is primarily the ocean.

Figure 4 indicates an exceptionally straightforward pattern in the distribution of zinc. It would seem that the primary source of the zinc is the Delaware River. This is not hard to believe for two reasons: 1) the high concentration of heavy industry in the vicinity of Philadelphia, and 2) the prevalence of economic zinc ore deposits in the Delaware drainage basin, most notably the huge deposit in Franklin, New Jersey.

Figure 5 appears to indicate a predominantly seaborne source for chromium, although high values in the upper reaches of the area would suggest that there is also a substantial contribution from the Delaware River. This also appears to be the case in Figure 6, illustrating the distribution of copper in the Bay. Figure 7 indicates that most of the lead in Delaware Bay sediments has its source in the Delaware River, and that there is a substantial amount of mixing in the middle reaches of the bay.

Although the data which comprise Figure 8 are the most suspect in this report, it would appear that there is a cogent story to be gleaned from the regional distribution of cadmium. It seems that the principle source is the Delaware River, and that the mixing which occurs in the lower and middle areas of this study has created a "sink" of cadmium in the vicinity offshore from the points of entry into the Bay of the Murderkill and St. Jones Rivers.

Judging by the distribution pattern for mercury in Figure 9, there is no doubt that the primary source of mercury is the Delaware River. Here again, mixing is occurring in the middle and lower reaches of the study area, although more restricted mixing than that experienced with cadmium. The same "sink" is also shown in Figure 9.

Figure 10, illustrating the distribution of trace nickel, indicates a primary source for nickel in the Delaware River, with a very straightforward distribution pattern. In Figure 11 one also sees a very straightforward pattern, although one which would indicate that the source of strontium in the Bay is the ocean with some limited mixing into the ebb tide side of the Bay along the Delaware shoreline.

In trying to answer the question of how much of any one of these metals is dangerous, toxic or lethal, one is hard pressed to quote rock-solid figures, even to the point of not wishing to hazard a guess. So little is currently known about the biochemistry of trace metals, that it is impossible to state what the danger levels are. One hopes that work on this type of an environmental problem is being pressed with all possible speed.

CONCLUSIONS

1) Trace metal geochemical aspects of the sedimentary environments which support oysters in Delaware have been typified for ten common trace metals. It is hoped that further work may

be accomplished in the foreseeable future which will expand the results of this work.

- 2) The two hypotheses mentioned in the <u>BACKGROUND</u> section of this report have been tested, and have been found not to be mutually exclusive. That is, both of the processes mentioned appear to be in operation. Fine-grained materials are being eroded from the tidal marshes and are accumulating in the near-shore bay area, where there are consistently low geochemical measurements. There also exist conditions for the preferential deposition of fine-grained materials carried into the Bay by the Delaware River, although their deposition does not occur where originally hypothesized.

 Deposition of river-borne materials occurs near the middle of the navigational channel, and up to the New Jersey side of the Bay in the uppermost reaches, and then approaches the Delaware side of the Bay in the area between Port Mahon and the Murderkill and St. Jones River mouths.
- 3) The characterization of the trace metals as to their primary source and the major factor influencing their distribution was made possible by Figures 2 through 11. It appears obvious that iron, zinc, lead, cadmium, mercury and nickel have their primary sources in the Delaware River, while magnesium, chromium, copper and strontium have predominantly seaborne sources. It also seems obvious that water currents are the principle factor influencing the distribution of all of these metals, irrespective of source area.

- 4) From Figures 5, 6, 7, and 11, it appears that there is a "hot spot" of high concentrations of chromium, copper, lead and strontium associated with the mouth of the Cohansey River in the northern extreme of the study area. Further investigation of this area should be undertaken to determine whether the area is a source for metal pollutants or a sink for metals borne by the Delaware River.
- 5) From Figures 2 through 11, it appears that there is a "sink" of trace metals being formed in the vicinity offshore from the mouths of the Murderkill and St. Jones Rivers. Further investigation of this area should be undertaken in order to ensure that shellfish taken from the region are within the U.S. Public Health Service limits of trace metals content.

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APPENDIX

Results of Emission Spectrophotometry, Reported in Parts

Per Million of the Finer than 63 Micron Sediment Fraction

SAMPLE ABBREVIATION KEY

Sample (from Table)	Sample Location
1	Bay Oyster Reef, B-1
2	Bay Oyster Reef, B-2
3	Bay Oyster Reef, B-3
4	Bay Oyster Reef, B-4
5	Bay Oyster Reef, B-5
6	Bay Oyster Reef, B-6
7	Bay Oyster Reef, B-7
8	Bay Oyster Reef, B-8
9	Bay Oyster Reef, B-9
10	Bay Oyster Reef, B-10
11	Bay Oyster Reef, B-11
12	Bay Oyster Reef, B-12
13	Bay Oyster Reef, B-13
14	Leipsic River West
15	Leipsic River East
16	Simon's Creek West
17	Simon's Creek East
18	St. Jones River West
19	St. Jones River East
20	Murderkill River East
21	Murderkill River West
22	Mispillion River West
23	Mispillion River East
24	Broadkill River West
25	Broadkill River East

"A" after a sample number indicates that it is a sediment sample from the finer than 63 micron fraction. "B" after a sample number indicates that it is a sample of dried and powdered oyster tissues from that location.

LOWER LIMITS OF DETECTION

Listed below are some of the lower limits of detection for some of the elements not listed in the accompanying table due to insufficient concentrations.

```
10,000 PPM:
             Li
 5,000 PPM:
             Dy
 1,000 PPM:
            As, Te, Ta, Tl, W
   500 PPM:
            Ga, In, Ra, Tb
  100 PPM:
            Hg, Sb, Pb, Mo, Th, Sn, V, Bi, Cd, Co
   50 PPM:
            Pt, Pd, Ru, Hf, Rh, Ir, Y, Lu, La, Se, Gd, Tm, Er
   10 PPM:
            Ge, Nb
    5 PPM:
            Au, Yb, Ho
    1 PPM:
            Вe
```

SAMPLE	r e	Mg	71	8 a	Mn	V	į.	Zn
13	> 100,000	28,086	10,000	1,000	50,000	1,000	1,000	10,000
16	1,000	5,000	100.	<100	100		10,000	50,000
24	> 160,00a	20,000	10,000	1,606	2,000	1,000	1.1650	100
29	3,000	10,000	360	<100	100		16,000	50,0LU
3A	70 W III	`						
58	3,130A:	10,096	300	4 100	200		16,835	30, 000
4,6	> 138,000	29,600	10.456a	1,600	2,000	1,000	≰1 ,060	300
48	3,000	5,400	300	∡ 1u0	1.00		10,000	30 ,000
11.7	▶1 60,069	29,88%	AU, Gun	1,600	2,000	1,636	£1,050	300
55	3,600	5,000	3 00	41 0€	1 01		10,640	5 0,008
56	>1 00,600	39,000	10,000	1,000	20,880	1,000	1,000	7,00G
ħŪ.	3,000	5,000	100	4 196	1400		10 ,000	56,000
7A	200,058	20,800	10,000	1,000	1,000	1,600	≰1 ,000	500
78	3,000	10,000	1:00	< 100	300		10,008	30,668
원되						******		
80	1,11111	14,868	1475	∠ 100	1 04.	~~=	16 th	1 s, that
9,5	≥1 00,000	20,000	10,000	1,000	1,000	1,000	∠1. 000	200
98	2 0,000	10,000	200	≰ 100	100		1 6,660	20,000
1.44		20,000	19,386	1,300	1 + 4 = 1	1,000	≟1 ,600	20a
108	0,000	13,800	2UG	∡ 159	100		10,000	26,588
117								w mw
119	2,000	19,000	200	▲100	3/16.		1 6,000	= 180,000
124	m=+ m							***
128	2,000	19,000	200	≮ £99	100		18,888	≥ 100,900
1.3A	≥ 100,686	15,600	lu, auto	1,000	1,000	1,000	≰1, 008	260
138	2,000	io,ooo	200	≼1 68 1	100		18, 088	16,600
144	100,000	t0,066	16,000	1,000	ace	1,000	∢1, 05€	<100
178	2,000	10,060	200	<100	1 00		10,000	≥ 106,006
15A	> 100,990	30,000	10,000	1,880	1,000	1,000	<1, 00G	<1 00
155	2,000	11,060	200	<100	100	~~~	10,000	≥ 106,000
16A	≥ 100,000	20,000	10,060	1,000	1,000	1,000	₫1,000	100
168	2,000	10,ដល់៤	200	< 100	100		10,600	≥1 00,000
17A	100,660	10,000	արա, ար	1,000	3 , 000	1,000	£1 ,000	268
178	2.000	10,000	100	<150	100			60,800
184	2100,000	20,00G	10,600	1,700	500		<1,000	260
188	5,588 • 100 000	2 0, 000	100	2 100	100		10.000	20,000
19A	≥ 100,880	20,000	16,688	1,000	800	1,000	≰1 ,000	200
198	50,000	26,886	200	41 00	100	•••	10,000	20,000
20A 20a	10. juil	30,000	16,686	800	588	1,000	41,000	∢1LO
208 216	5,0uli ∍rra oro	20,000 P	200	≺ 180	100		10,000	3,000
21ñ	> 186,368	26,538	10,000	1,500	2,000	1,000	< 1,030	<1 00
218	5, 09u	20,000	200	< 100	100		10,000	29,800
228 228	5,888	20,00u	 Data	2100	100			***
23A	7,000 180,600	10,000	200	≼ 100	160	3 OF 2	10,000	10,000
23A 23B	168,000 5,888	25,000	11.,000 200	1,66.6	1,600	1,000	<1,000	100
	2100,886		200 175 noo	<108	100	410.00	10,005	10,850
248	5,800	29,005		1,000	600		<1,900	√1 00
	დ,ნინ ⊵10 0,080	20,000 20,000	500 10 (00)	<100 1000	100	1 000	10,000	10,000
258	5,866	20,000 20,000		1,000	500		<1.0 60	200
6.00	J,000	շե, ասա	190	<1 00	100		10,600	16,000

SAMPLE ABBREVIATION KEY

Sample (from Table)	Sample Location
1	Bay Oyster Reef, B-1
2	Bay Oyster Reef, B-2
3	Bay Oyster Reef, B-3
4	Bay Oyster Reef, B-4
5	Bay Oyster Reef, B-5
6	Bay Oyster Reef, B-6
7	Bay Oyster Reef, B-7
8	Bay Oyster Reef, B-8
9	Bay Oyster Reef, B-9
10	Bay Oyster Reef, B-10
11	Bay Oyster Reef, B-11
12	Bay Oyster Reef, B-12
13	Bay Oyster Reef, B-13
14	Leipsic River West
15	Leipsic River East
16	Simon's Creek West
17	Simon's Creek East
18	St. Jones River West
19	St. Jones River East
20	Murderkill River East
21	Murderkill River West
22	Mispillion River West
23	Mispillion River East
24	Broadkill River West
25	Broadkill River East

"A" after a sample number indicates that it is a sediment sample from the finer than 63 micron fraction. "B" after a sample number indicates that it is a sample of dried and powdered oyster tissues from that location.

LOWER LIMITS OF DETECTION

Listed below are some of the lower limits of detection for some of the elements not listed in the accompanying table due to insufficient concentrations.

```
10,000 PPM: Li
5,000 PPM: Dy
1,000 PPM: As, Te, Ta, Tl, W
500 PPM: Ga, In, Ra, Tb
100 PPM: Hg, Sb, Pb, Mo, Th, Sn, V, Bi, Cd, Co
50 PPM: Pt, Pd, Ru, Hf, Rh, Ir, Y, Lu, La, Se, Gd, Tm, Er
10 PPM: Ge, Nb
5 PPM: Au, Yb, Ho
1 PPM: Be
```

SAMPLE	Pb	В	Cr	Ni	Cu	Sn	Ga	Co	Νb	L.a	Ag
1A	2,000	100	800	1,000	500	100	500	500	≦ 10	5 0	1
18		10	∢ 100	41 00	2,000						100
2A	800	100	500	200	200	100	500	100	<10	50	1
28		10	41 00	< 100	2,000						100
3A											~
38		10	~ 100	<100	3,000						100
ЦĄ	800	100	300	20G	200	100	500	100	<10	50	1
4B		≤ 10	∢1 00	< 100	1,000				***		100
5A	800	100	500	200	200	100	500	100	< 10	50	₹1
58			<100	◄ 100	2,000	100					100
6A	1,000	100	500	500	300	100	500	100	<10	50	, 1
6B		10	< 100	<1 100	3,006	700	# # # # C (1) (2)	***			100
7A	200	160	500	200	500	100	500	100	≤ 10	50	1 50
7B			<100	<100	1,005						50
88	*	7.0	100	#	1 OOO						50
88	700		< 100	≪ 100	1,000	100	enn	100	≰ 10	E(:	
9A	200	188	500	200	500 500	100	500	100		5ជ	≰ 1 10
9B	200		≺ 100	< 100	500 200	100	500	100	 ≰10	50	≰ 1
10A	200	100	500 -100	200	300 500	າບຕ		100	≖ t⊓		10
108		10	< 100	<100	500						+++
11A		10	100	4100	9 00N		**-				100
118		18	< 700	<100	2,000						
12A		1.7		<160	1 000						100
128	25ū	10 100	<10L 500	150	1,000 250	100	500	100	£ 10	5()	1 1 1
13A 138	250	10	≼ 106	∢ 100	1,000	100	500	100	====		10
14A	100	100	200	200	200	< 100	500	100	< 10	50	41
148	100		< 100	< 190	1,000		***	100			100
15A	200	100	500	200		< 100	500	100	≼ 10	5 U	<1
158		19	≺ 108	< 1üÜ	1,000		700	100			100
16A	300	100	400	260	500	100	500	100	∠ lu	50	1
16B		10	< 100	< 100	1,000						100
17A	400	100	400	2u0	500	100	500	100	< 10	5 0	1
178		10	< 100	≰ 100	1,000						50
18A		100	500		1.000	100	500	106	4 10	50	<1
188		10	< 100	≤100	500						10
19A	200	160	500	200		≤ 100	500	100	≤ 10	50	2
198		10	∡ 100	≰ 100	500						10
2LA	200	100	200	200	1,000	100	500	100	< 10	50	< 1
26B		10	∢ 100	<188	200						1ບ
21A	200	100	500	200	200	100	500	100	<10	50	< 1
218		10	< 106	< 100	500						10
22A											
228		10	< 100	< 100	500	[10
23A	200	160	200	200	200	<1 00	5 00	100	< 10	50	<1
238		10	< 100	< 100	1,000						20
24A	200	100	200	200	100	< 100	500 .	100	≪ 10	50	<1
248		10	<0.00	< 100	500						20
25A	200	100	500	200	500	100	500	100	≰ 10	50	1
258		30	₹ 700	< 100	500					4	10